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MECHANISMS OF ANTIOXIDANT ACTION

EFFECT OF THE POLYMER MEDIUM ON THE ANTIOXIDANT EFFICIENCY OF THE DITHIOLATES

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Abstract—Peroxide decomposing antioxidants (e.g. nickel dithiophosphates and thiophosphoryl disulphides) control hydroperoxide formation during processing and on exposure to light. However, these additives are more efficient u.v. stabilizers in polypropylene (PP) than in low density polyethylene (LDPE). It is suggested that this difference results from the more rapid formation of hydroperoxides in the more oxidisable substrate under normal processing conditions. In contrast, nickel xanthates are completely destroyed in PP under the same processing conditions and the transformation products obtained in this case are less effective u.v. stabilizers than the original xanthates. Nickel dialkyl dithiophosphates stabilise both LDPE and PP very effectively, while nickel alkyl xanthates are much less effective u.v. stabilisers in both matrices. However, the difference between the efficiencies of the two dithiolates is much less in the case of LDPE. The nickel dithiophosphates and xanthates effectively synergise with the commercial u.v. absorber Cyasorb u.v. 531 (HOBP) but they show antagonism towards a typical chain breaking antioxidant, Irganox 1076, during u.v. exposure. They are however synergists under thermal oxidative conditions.

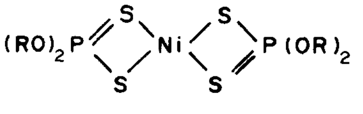
INTRODUCTION

The mechanism of antioxidant action of metal dithiolates both in model compounds and in polymer substrates has been discussed in earlier papers [1–6]. We have recently compared the effectiveness of nickel dithiophosphates (NiDRP) and nickel xanthates (NiRX) and their corresponding disulphides as u.v. and thermal stabilisers in low density polyethylene (LDPE) [7]. The main mechanism of action of both nickel complexes and disulphides is the catalytic destruction of hydroperoxides by a non-radical ionic mechanism. The purpose of this study is to investigate the effect of a more oxidisable substrate, polypropylene, on the effectiveness of these dithiolates as u.v. stabilisers and the effect of processing conditions on their final performance both as u.v. and thermal stabilisers. The effect of their combination with a typical chain breaking antioxidant is also studied.

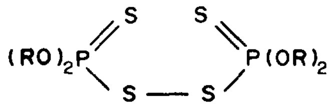
EXPERIMENTAL

Materials

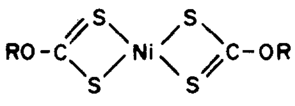
Unstabilised polypropylene was supplied by Imperial Chemical Industries Ltd as propathene HF20C CV170. Nickel complexes of thiophosphoric acid (NiDRP, I) and xanthic acid (NiRX, III) and disopropyl thiophosphoryl disulphide (DiPDS, II) were prepared by known procedures [8–10]. 2-Hydroxy-4-octyloxybenzophenone (HOBP, IV) and the phenolic antioxidant *n*-octadecyl-3(3′,5′-di-tert-butyl-4-hydroxyphenyl) propionate (Irganox 1076, V) were supplied by American Cyanamid and Ciba-Geigy, respectively.



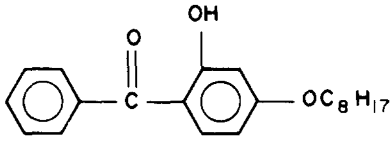
(I) NiDRP



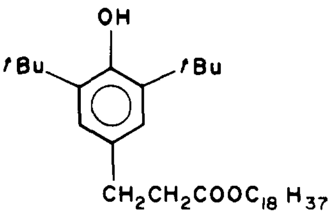
(II) DRDS



(III) NiRX



(IV) HOBP



(V) Irg 1076

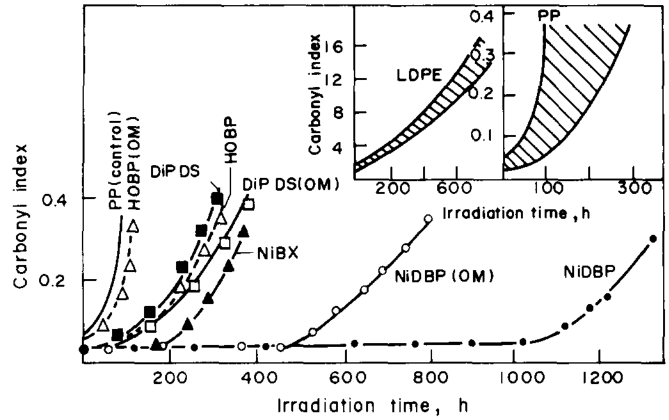


Fig. 1. Effect of mixing procedure (processing in closed mixer (CM) and open mixer (OM)) on photo-oxidative stability of PP containing additives (2.5×10^{-4} mol/100 g). Inset compares photostabilising effectiveness of mildly processed (CM, 10) DiPDS in LDPE and PP.

Processing of PP and compression moulding into films (8") in the presence and absence of additives (processing in the RAPRA Torquerheometer at 180° in a closed or open mixer) and the subsequent irradiation and thermal ageing of the polymer films was carried out as described previously [2]. I.R. spectra were recorded with a Perkin-Elmer 457 spectrophotometer and carbonyl index was measured as described previously [2]. U.V. absorption spectra were recorded in a Pye-Unicam SP-800.

RESULTS

Unstabilised PP has a much shorter u.v. lifetime than similarly processed unstabilised LDPE. The concentration of PP hydroperoxides formed during processing has been shown [5] to be much higher than that found in LDPE under similar conditions. Moreover, the kinetics of formation and disappearance of hydroperoxides during the early stages of photo-oxidation of the two polymers are also different; in contrast to LDPE where the hydroperoxides initially present decay rapidly to undetectably low values, the hydroperoxide concentration in PP increases rapidly to a maximum during the first 30 hr of u.v. exposure prior to its decay.

Table 1. Comparison of u.v. stabilisers in PP

Antioxidant	U.V. EMT (hr)§	
	Observed	Calculated*
Control (no additive)	90	—
HOBP†	835	—
HOBP	295	—
1076	420	—
DiPDS	285	—
DiPDS‡	400	—
NiDBP	1370	—
NiDBP‡	780	—
NiBX	360	—
DiPDS + HOBP†	1470	1120
NiDBP + HOBP†	3000	2205
CuDIP + HOBP†	1800	—
NiBX + HOBP†	2450	1195
DiPDS + 1076	400	700
NiDBP + 1076	1400	1790

* The effect of synergist or antagonist calculated on additive bases.

† 5×10^{-4} mole/100 g.

‡ Processing in an open mixer for 10 min at 180°.

§ U.V.—Embrittlement time.

Concentration of additives 2.5×10^{-4} mole/100 g. Unless stated otherwise all processing times are 10 min in a closed mixer at 180°.

The stabilisation of LDPE by nickel dithiolates (e.g. NiDRP and NiRX) and their corresponding disulphides has been discussed [7]. Very significant differences were observed when the same stabilisers were studied in PP. Figure 1 shows the effect of the mixing procedure on the photo-oxidative stability of PP containing NiDBP (**I**, R = Bu) and DiPDS (**II**, R = iPr) and a commercial u.v. stabiliser, HOBP. It is clear from this figure that increasing the severity of processing adversely affects the photo-oxidative stability of PP containing NiDBP and HOBP whereas a thiophosphoryl disulphide (DiPDS) becomes more effective with increasing oxygen access in the mixer (see Table 1). This general behaviour resembles the performance of the same stabilisers under similar conditions in LDPE. However, a major difference is that the amount of NiDBP left after processing in PP is much less than that remaining in LDPE at the same

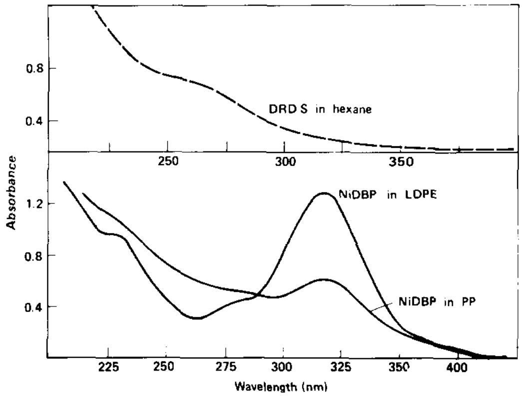


Fig. 2. Comparison of u.v.-absorption spectra of NiDBP (2.5×10^{-4} mol/100 g) in LDPE and PP after processing in a closed mixer for 10 min. Solution spectrum of DRDS (**I**, R = *n*Bu) in hexane is also shown.

Table 2. Changes in concentration of NiDBP after processing in PP (180°) and LDPE (150°)

	(NiDBP) × 10^{-4} M/100 g		
Polymer	Before processing	Left after processing (CM, 10)*	PIP† (hr)
LDPE	2.5	2.3	1200
PP	2.5	0.95	1050

* Processing in a closed mixer for 10 min.

† Photo-oxidation induction period.

initial added concentration and under the same processing conditions (apart from temperature, 180° for PP and 150° for LDPE). Figure 2 and Table 2 demonstrate this. Figure 2 compares the u.v. spectra of NiDBP at the same concentration and after a similar mixing procedure (CM, 10) in both LDPE and PP. The spectrum of NiDBP in LDPE is exactly the same as its spectrum in hexane solution and shows that a much smaller part of NiDBP is consumed during processing in LDPE compared to that in PP. Further, in the case of PP the spectral characteristics of NiDBP differ from those for its hexane solution below 275 nm (The corresponding disulphide, however, absorbs broadly in this region, see dotted curve—Fig. 2). The greater loss of NiDBP (Table 2) and the change in its spectral characteristics in PP samples is attributed to the higher processing temperature and the more oxidisable substrate. Under these conditions more conversion of the nickel-complex to the corresponding disulphides and its oxidation products is to be expected. These products must therefore be responsible for the marked increase in the absorption below 270 nm (the disulphide (**II**) absorbs broadly in this region) (Fig. 2).

An interesting observation in the case of the PP stabilized with NiDBP however is that, although less than half the originally added nickel survived the processing operation, this small concentration remained for an unexpectedly long time during u.v. exposure, thus providing a very long photo-oxidative induction period, PIP. The length of PIP (Fig. 1) for a stabilised PP film is the same as that for LDPE stabilised with the same initial concentration of NiDBP under the same mixing conditions, although the actual concentration surviving the processing operation in the case of PP is much less. In effect, therefore, the NiDBP remaining after processing stabilises PP much more effectively than might have been predicted on the basis of its behaviour in LDPE.

The inset of Fig. 1 shows that DiPDS also has a greater photostabilising effectiveness in PP compared with its performance in LDPE. Mildly processed PP containing DiPDS shows an appreciable photo-oxidative stability whereas stabilised LDPE (compared the two envelopes in inset of Fig. 1) shows only a small improvement relative to the LDPE control.

In the case of the xanthates NiRX (**II**, R = Et, Bu) even mild processing (CM, 5) precludes the survival of the nickel complex. Thus, instead of the characteristic u.v. absorption of NiRX a new absorption emerges in the region of 278 nm (Fig. 3). Processing of PP with CuEX under identical conditions revealed the same new absorption feature. NiBX, therefore, gives only a short PIP (150 hr, see Fig. 1) and hence a short film lifetime (Table 1). The difference in the photostabilising effectiveness of NiDRP and NiRX in PP is much more pronounced than the difference in LDPE.

Nickel dithiophosphates and xanthates synergise effectively with the commercial u.v. absorber HOBP in PP, Fig. 4 and Table 1, in a way similar to that observed previously for NiDRC [5, 6]. DiPDS also shows very effective synergism with a definite photo-induction period although neither stabiliser alone give a PIP in PP.

In the presence of a hindered phenolic antioxidant (e.g. Irganox 1076), NiDRP and NiRX show antagonistic effects in PP during u.v. exposure, (Fig. 5, Table 1), whereas they synergise with the same phenol during heat ageing (at 140°) as shown in Fig. 6 and Table 3. This behaviour resembles the behaviour of the closely related dithiocarbamate complexes [5]. DiPDS which is also a good peroxide decomposer, also antagonises with Irg. 1076 under u.v. ageing conditions (see Figs 5 and 6).

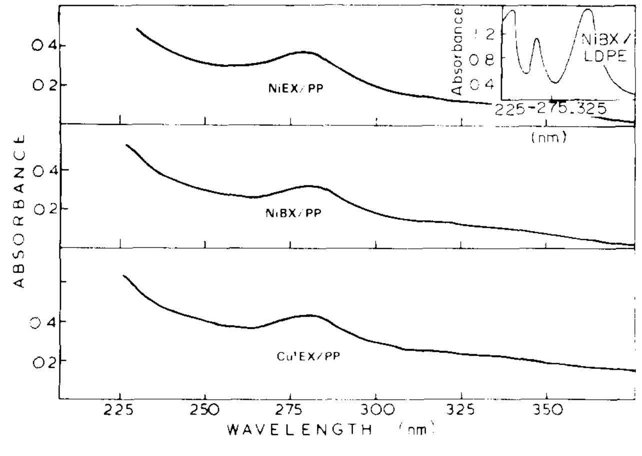


Fig. 3. U.V. absorption spectra of xanthates (2.5 × 10^{-4} mol/100 g) in PP after processing in closed mixer for 5 min. Inset shows absorption spectrum of NiBX processed in LDPE under the same mixing procedure and at the same initial concentration used for PP.

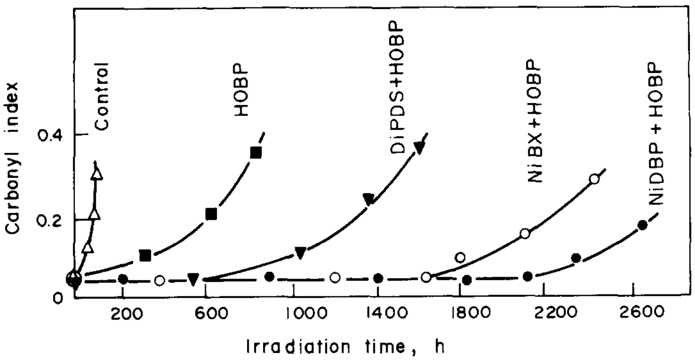


Fig. 4. Synergistic effect of dithiolates with HOBP in PP processed at 180° in closed mixer for 10 min. Concentration of each additive is 2.5×10^{-4} mol/100 g.

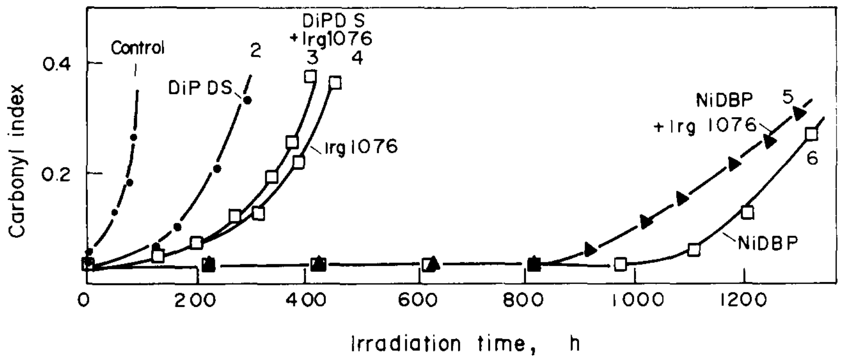


Fig. 5. Effect of dithiolates, in the presence and absence of Irganox 1076, on the photo-oxidative stability of PP processed at 180° in a closed mixer for 10 min. Concentration of each additive is 2.5×10^{-4} mol/100 g.

DISCUSSION

Nickel dithiolates are rather unstable at the high processing temperatures used for PP. Severe processing is therefore, detrimental to the parent complexes. The photostabilising activity of the complex is almost halved by processing in an open mixer (Fig. 1 and Table 1). By contrast, the corresponding disulphides, at the same initial molar concentration and the same processing conditions, become almost twice as effective (Table 1). The mode of action of the antioxidant in this case must therefore be directly related to the amount and nature of oxidation products formed since PP processed in the presence of the disulphide at 180° in an open mixer was found to be consistently more photo-oxidatively stable than that processed in a closed mixer. The same phenomenon has been ob-

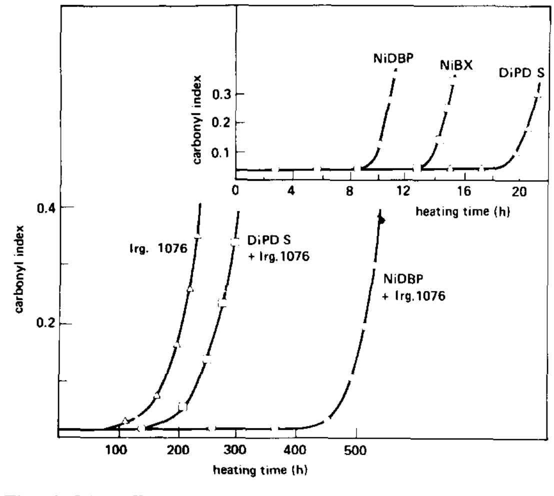
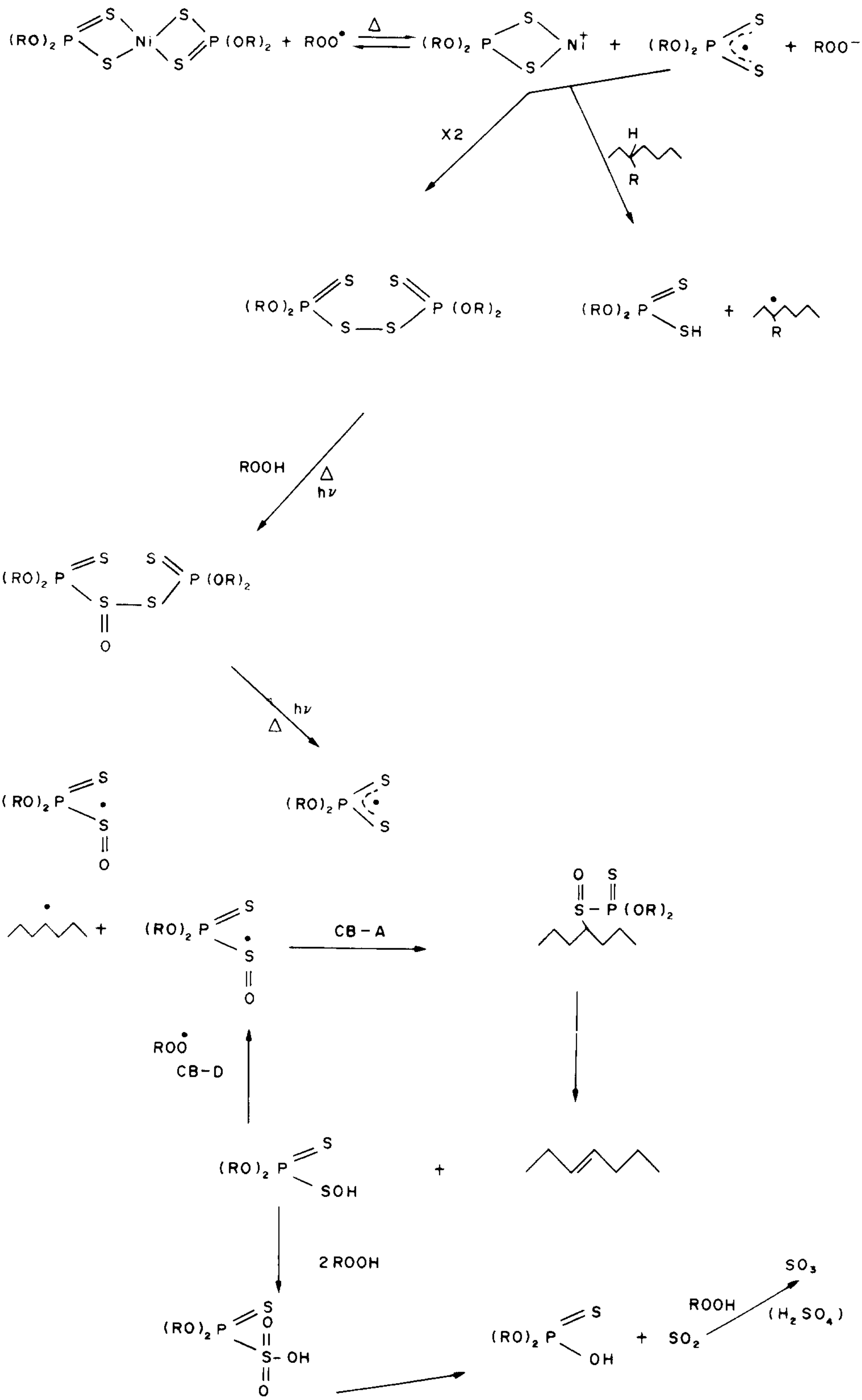


Fig. 6. The effect of additives on the thermal oxidative stability of PP at 140° (flow rate of air $2.5\,\mathrm{cm}^3 \cdot \mathrm{min}^{-1}$). Concentration used 2.5×10^{-4} mol/100 g.

Table 3. Effect of thermal oxidation (at 140° on the lifetime of PP films containing 2.5×10^{-4} M/100 g of the appropriate antioxidant

Antioxidant	Embrittlement time EMT (hr)	
	Observed	Calculated*
Control (no additive)	1	—
1076	230	—
DiPDS	24	—
NiDBP	18	—
NiBX	20	—
DiPDS + 1076	300	254
NiDBP + 1076	540	248

* The effect of synergist calculated on additive basis.

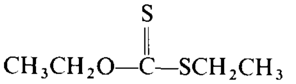


Scheme 1. Regenerative mechanism for stabilisation of PP

served for LDPE [7]. The outstanding photostabilization afforded by NiDBP when present alone in PP films (Fig. 1) cannot be explained only on the basis of the residual complex surviving the processing operation. However, the presence of even quite small amounts of the complex seems to be essential to the photostabilisation process. The nickel complex therefore not only acts as a reservoir for the slow and controlled release of the antioxidant active oxidation products, but it also exerts a positive protective effect on the derived products.

The metal complexes (e.g. Ni^{II}, Cu^{I}) of xanthic acid behave differently. In this case the nickel complexes are found to be completely destroyed even after very mild processing operation (Fig. 3). The relative instability of NiRX towards higher processing temperature (180°) together with the high oxidisability of PP is expected to lead to higher yields of dixanthogens as in the case of NiDRP. Evidence that the dithiocarbonic moiety becomes partially bound to the polymer has been presented previously [2]. The evidence supports the formation of dixanthogen type moiety.

The u.v. absorption band formed when NiRX or CuRX were processed with PP at 180° had similar characteristics (max. = 278 nm) to that of esters with structure (**I**) reported in the literature (**II**) indicating



$$CH_3CH_2O{-}\overset{\overset{S}{\|}}{C}{-}SCH_2CH_3$$

(**I**)

the formation of a xanthate ester during processing, presumably via the intermediate disulphide [2]. The rapid exhaustion of the nickel complex and the associated formation of the above ester is reflected in the lower photostability of xanthate stabilised PP than dithiophosphate stabilised PP. The much higher antioxidant efficiency in the case of the dithiophosphate in PP as compared with LDPE indicates the presence of antioxidant active secondary products in the presence of the nickel complex.

It has been shown [6, 12] previously that HOBP is an indifferent antioxidant during processing and behaves essentially as a screen during the very early stages of photo-oxidation when hydroperoxides are the primary photo-initiators. Severe processing of PP containing HOBP reduces the effectiveness of the latter as a u.v. absorber (see Fig. 1). The fact that HOBP is unable to destroy or inhibit the formation of hydroperoxides during processing and during subsequent u.v. exposure, contrasts with the peroxidolytic ability of both the dithiophosphates and the xanthates. The synergism resulting from the combination of any of these peroxide decomposers with the u.v. absorber, HOBP, is therefore in part due to minimisation of the deleterious effects of hydroperoxides formed during processing on HOBP. On the other hand, HOBP exerts its effect during u.v. irradiation by prolonging the presence and hence the activity of the nickel dithiolates [12]. Neither HOBP or DiPDS when used alone give a PIP, but the synergistic combination has a definite induction period (Fig. 4). The period of inhibited photo-oxidation shown by the synergistic system must therefore be partly due to the protection of the disulphides (or their oxidation products) from photolysis and partly due to the protection of HOBP from photo-oxidative destruction in the presence of peroxides. The antagonism of both NiDBP and DiPDS with the hindered phenol, Irganox 1076, (Fig. 5, Table 1) is similar to that occurring with the dithiocarbamates. In the latter case it was suggested that the phenol or its quinonoid oxidation products photosensitises the decomposition (or oxidation) of the dithiocarbamates [5], and a similar explanation may be invoked here.

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